May 12, 1970 M. HOBERMAN ET AL 3,512,049

ELECTROLYTIC TIMER

Filed Feb. 28, 1968

FIG. 1

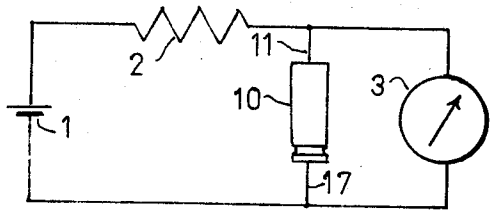


FIG. 2

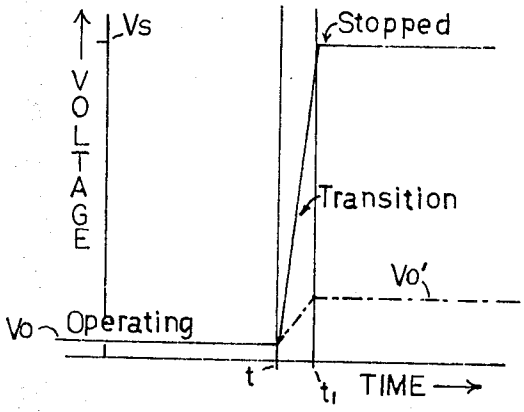


FIG. 3

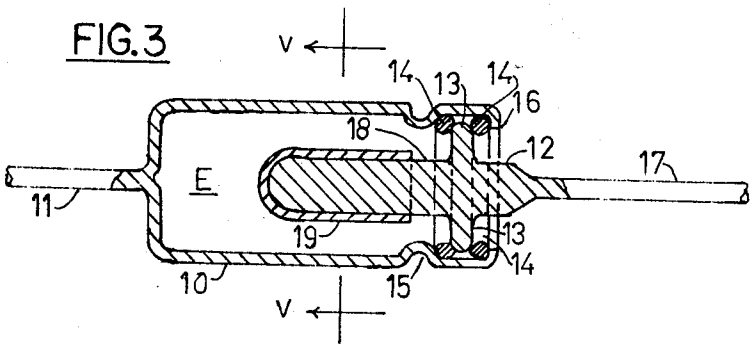


FIG. 4

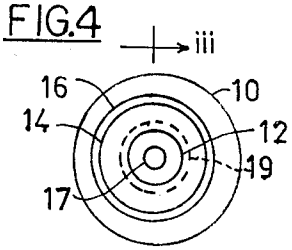


FIG. 5

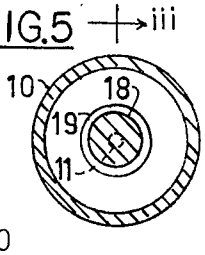


FIG. 6

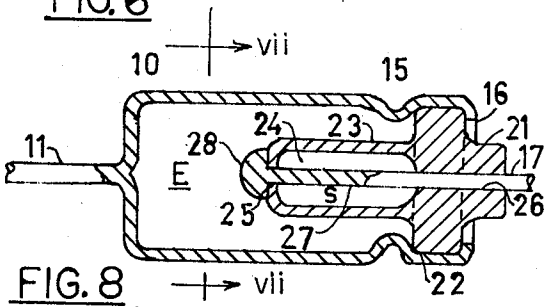


FIG. 7

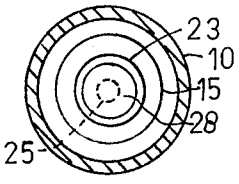


FIG. 8

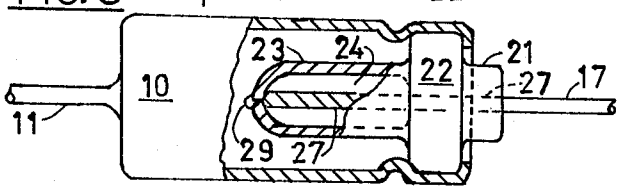
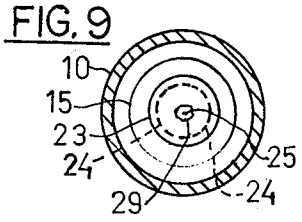


FIG. 9



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United States Patent Office 3,512,049 Patented May 12, 1970

3,512,049

ELECTROLYTIC TIMER

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Filed Feb. 28, 1968, Ser. No. 708,970
Int. Cl. H01g 9/00
U.S. Cl. 317—230 4 Claims

ABSTRACT OF THE DISCLOSURE

An electrolytic timing cell is arranged so as to cover the anodic substrate with a passivated surface layer, insulating cover or liquid, so that the cell, after plating a predetermined quantity of anodic material, will increase in resistance more rapidly and to a higher value, reducing any tendency to produce gas and interposing a high resistance anodic surface layer.

This invention relates to electrolytic timing cells or coulometers, and more particularly to such cells in which elapsed time is measured by the plating of an anodic material.

One of the early uses of such devices was in the acceleration integrator of the German V–2 missile, in which the depletion of anodic silver chloride produced a cell functioning as a battery to produce an E.M.F. which signaled the occurrence of the condition to be sensed by the cell. In the nature of the case, the behavior of the cell thereafter was of but little interest. In later electrolytic timers, where the cell might remain in circuit after exhaustion of the predetermined quantity of anodic material, it has been found important to produce a large rise in the voltage drop across the cell in order to activate voltage operated auxiliary devices.

A well designed cell will have (under given conditions as to temperature, applied voltage, etc.), a substantially constant resistance while the anodic material is plating and a higher resistance thereafter. In between, the resistance may rise due to partial removal of anodic material producing partial exposure of substrate, followed by a further rise as the anodic ions remaining in the electrolyte are cleared out, following the complete exhaustion of the anodic material from the anode itself. The result of such transitional phenomena is to lessen the sharpness of the resistance change and hence to increase possible error in the precise time of operation of the cell. It is an object of the invention to lessen the transition time and increase the magnitude of the change of resistance and thereby increase the accuracy of the cell.

While the invention in its broader aspect is applicable to visual indicating cells and to cells adapted to measuring the elapsed time, as distinguished from those which merely indicate the end of a predetermined interval, its advantages are realized most fully in miniature, one-shot, electrically operating cells, and it is an object of the invention to provide a cell structure and operation which permit the production of such cells economically and with a high degree of reliability and accuracy.

With the foregoing objects in mind, as well as others which will appear in the course of the following description, the invention will now first be described with reference to a preferred embodiment, as illustrated in the accompanying drawing, and the features forming the invention will then be pointed out in the appended claims.

In the drawing:

FIG. 1 is a schematic simplified circuit diagram;

FIG. 2 is an operating curve;

FIG. 3 is an axial section, taken on line *iii—iii* of FIG. 4, of the cell of the invention;

FIGS. 4 and 5 are, respectively, an end elevation and section on the line *v—v* of FIG. 3;

FIGS. 6 and 7 are, respectively, an axial section and section on the line *vii—vii* thereof, of a modification; and

FIGS. 8 and 9 are, respectively, a view partly in central axial section and partly in elevation and a section on the line *vii—vii*, showing the cell of FIGS. 6 and 7 after plating of the anodic material.

Referring now to FIG. 1, the leads **11**, **17** of the timing cell (casing **10**) are shown as connected through a voltage dropping resistor **2** to an E.M.F. indicated by the battery **1**. A meter **3** reads the voltage across the cell. So long as the cell has not consumed a predetermined quantity of anodic material, the voltage across it will remain at a substantially constant low value (*Vo* in FIG. 2), which voltage will be the voltage across the source **1** less the voltage across resistor **2** ($I \times R$). Once the anodic material is exhausted, the current drops, as also the voltage drop across resistor **2**, so that the voltage across the cell rises and may approximate that of the source **1**. However, the permissible "stopped" voltage across the cell cannot be permitted, in many applications, to remain for any length of time above the value at which dissociation of the electrolyte and gas formation occur. This value is ordinarily about 0.7 volt, or less. Cells, as heretofore constructed with an insoluble (e.g., gold plated) substrate supporting the anodic material still have a fairly low resistance, corresponding to a voltage drop such as indicated by the dot-dash line *Vs'* in FIG. 2, and a comparatively gradual transition from the operating voltage drop *Vo*. A cell constructed according to the present invention may have a very much increased "Stopped" voltage *Vs* and much sharper transition.

A preferred type of cell is shown by way of example in FIGS. 1 to 3. The envelope or casing **10** is preferably formed from conductive metal (e.g., copper), and serves as the cathode, being provided with a lead **11** for connecting the cell to another conductor or circuit element. The anodic member **12** of the cell has a radial flange **13** for securing and sealing it into the cell envelope **10**. As shown in FIG. 3, the flange periphery is held in position axially and radially, and in spaced relation to the wall of the envelope **10** by means of a pair of O-rings **14**, which are compressed against the flange **13** and inside of the wall of envelope **10** by the narrowed neck **15** and turned in rim **16** of the envelope **10**. As will be apparent to those skilled in the art, the manufacture of the member **10** and its assembly with anodic member **12** involve only standard and economical mass production procedures.

Anode **12** has a connecting lead **17** and extends into the envelope **10** as indicated at **18**. By spacing the anode section **18** properly from the envelope inner surface, an even deplating action can be obtained so that the anodic material **19** (e.g., copper) carried on section **18** is removed from all parts thereof at about the same time. The portion of the anode member section **18** and flange **13** which are not covered by the anodic material **19** may be passivated so as to be rendered non-conductive or may be coated with a non-conductive varnish.

The anodic member **12** generally is conductive, apart from its surface wherever passivated or coated with insulating material, and the voltage drop across the interface between section **18** and the anodic material **19** is negligible. The material of the anodic member, or at least the surface of section **18** thereof, is such, however, that as the section **18** is exposed to the electrolyte by removal of anodic material **19**, its surface is passivated and forms a high resistance coating which also resists further attack by the electrolyte. The anode may be

formed of a variety of metals, including aluminum, tantalum and titanium, tantalum being the preferred metal for use as the anodic member or substrate in the cell of the invention. In any case, exposure of the substrate metal to the electrolyte will anodize the metal, producing an electrically insulating surface thereon, which inhibits any further current flow through the cell. In making the anodic member, the tantalum is first formed into the shape shown, and the part of the extension **18** which is to be covered by the anodic material **19** is then scraped, ground or abraded to remove the surface oxide layer, while submerged in an inert fluid such as alcohol or in an inert atmosphere. While still protected by an adhering layer of the alcohol or by other inert fluid or gas, the member is made the cathode of a plating bath and has a predetermined quantity of the anodic material plated onto it, this being accomplished before any substantial reformation of oxide coating can occur.

The anodic material thus plated onto the anodic member is preferably copper, as also is the cathode member **10** of the timing cell. A suitable electrolyte (E in FIG. 3) may consist of water, phosphoric acid and a copper salt. The phosphoric acid content of the electrolyte exceeds 50% concentration and the copper salt may be copper phosphate, copper pyrophosphate or copper carbonate. the electrolyte solution may be prepared by heating the phosphoric acid solution to 75° C. and dissolving the copper salt in it. Copper metal is then added and the solution is maintained at 75° C. until no more copper dissolves. After filtering, it is ready for use.

The cell of the invention may be made with a glass or other transparent envelope, and may also be arranged for reading the elapse time at intermediate values, in addition to the terminal value. The cell construction and proportions may also be varied, as well as the manner of connecting it into a circuit, as by substituting for the wire leads **11**, **17** prongs adapted to be plugged in suitable spring sockets. The preferred form, however, is generally as described above, utilizing a drawn or extruded cathode which also serves as the container for the electrolyte. The size of the cell is also varied to suit the requirements of particular applications, but a cell having a diameter of about one quarter inch will be found suitable for a wide variety of uses.

One typical use for the cell is as a switching device, a transistor or relay being substituted for the meter **3** of FIG. 1. In this case, when the controlled operation has continued for a predetermined time the cell functions to switch off the power, thus terminating the operation, or may switch over so as to initiate another operation.

Another typical use of the cell is to indicate an expiration of predetermined operating time, and in this case, a neon lamp may be substituted for the meter **3** of FIG. 1. The circuit may be arranged so as to measure a chronological time interval or so as to measure the time integral of any desired quantity. Missiles, satellites, detonating devices and automatic equipment of a great many kinds involve uses of this type. The cell affords improved accuracy and also permits uses where it is left in place indefinitely in the "stopped" condition, due to its high stopped resistance and a consequent ability to take high "stopped" voltages without causing dissociation of the electrolyte and accompanying production of gas.

Another use for the cell is the measurement of the lapse of guaranteed operating time. For example, the cell may be connected to the wiring of a motor vehicle or appliance of various kinds, the object being to measure either the lapse of a given period of operating time or the integral of a quantity representing rate of use. Thus, the cell may be connected through a dropping resistor to the battery of a car, whenever the car switch is turned on to a driving position. The cell will then indicate the expiration of a predetermined number of driving hours, which may be made the expiration period for a guarantee. The cell may also be connected to read a

voltage proportional to speed of the engine or vehicle, thus providing for a guarantee period which depends upon the operating speed. In a particular case where the proportionality is direct, the interval measured will, of course, be the distance driven. The running out of the allotted time or service period may operate any desired signal or switch device, and, in cases such as just mentioned, may take place without any obvious indication whatsoever, the cell remaining in place unless and until a check on the service period is required, and this is readily accomplished by reading the cell resistance. If no such reading is required, the cell may remain in place indefinitely and require no provision to protect against gas production, even though subjected to a comparatively high voltage, as, for example, several volts in the automobile use discussed above.

The cell of the invention is adapted to withstanding severe shock and vibration conditions, as required in many missile and other applications, and is also adapted to use over a wide temperature range, such as from −55° C. to +71° C. The cell can be made in convenient capacities, such as, for example, one, five, twenty or fifty hundred microampere hours, (0.0001, 0.0005, 0.0020 or 0.0050 ampere hour), and stored and used as required, a shelf life in excess of ten years being obtainable.

FIGS. 6 to 10 show a modified form of the invention. In this form, the anode element **27–28** may be composed entirely of the platable material, such as copper, and is supported in an inert plastic member **21** which insulates most of the anode from the cathodic shell **10** and from the electrolyte E therein. Member **21** may be made of Teflon, polyethylene, or any other plastic having suitable mechanical and electrical properties. Member **21** is held and sealed in casing **10** by the enlarged section or flange **22** and has a shaft **23** extending into the interior of the cell and having a hollow center **24**. The anode **27** passes through member **21**, fitting in sealing relation to the passage **26** at one end of the space **24** and to the sphincter **25** (needle hole or slit) at the other end thereof. Anode **27** preferably terminates in an enlarged end **28** containing most of the metal to be plated. When the anode has been plated away so as to remove the enlargement **28**, the sphincter **25** is permitted to close around the end of the remaining part of anode **27**, insulating against further current flow. The space **24** may be filled with an inert material such as a silicone oil or grease, which may ooze out slightly, forming a bead **29** which assists in insulating the space **24** and anode **27** from the electrolyte E, thereby producing an effect similar to the coating formation in the embodiment of FIGS. 3 to 5.

What is claimed is:

1. A sealed coulometer timer cell comprising a cathode, an anodic element and an electrolyte contacting the cathode and anodic element, a quantity of material selectively platable electrolytically on either said cathode or anodic element, and means operable upon deplating a predetermined part of said material from the anodic element for covering the surface exposed thereby with an electrically insulating layer.

2. A sealed coulometer timer cell according to claim **1**, in which the anodic element comprises a substrate of conductive metal and said quantity of material comprises a predetermined amount of a different metal carried on said substrate, and the said substrate metal reacts with the electrolyte to form an anodized electrically insulating surface layer, whereby exposure of the substrate by deplating the said different metal results in the formation of said layer.

3. A sealed coulometer timer cell according to claim **2**, in which the substrate is tantalum, the said different metal is copper and the electrolyte is composed of phosphoric acid and a copper salt.

4. A sealed coulometer timer cell according to claim **1**, in which the anodic element comprises a shaft and a sphincter of insulating material surrounding the same in sealed relation thereto, the said predetermined part

of said material being immersed in the electrolyte and adjacent the sphincter, whereby deplating thereof permits closing of the sphincter to cover the remainder of the anodic element.

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JAMES D. KALLAM, Primary Examiner

U.S. Cl. X.R.

317—231